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PAPER AGING AND DEGRADATION: RECENT FINDINGS AND RESEARCH METHODS

María Cristina Area^{a,b,*} and Hervé Cheradame^c

Paper aging and conservation are matters of concern to those responsible for archives and library collections. Wood-derived fibers are mainly composed of cellulose, hemicelluloses, and lignin, but paper composition can also include additives, such as starch, minerals, and synthetic polymers. Therefore, paper is a multi-component material, and because of its complex and varied nature, research findings in paper chemistry can be difficult to interpret. Deterioration of paper is caused by many factors such as acid hydrolysis, oxidative agents, light, air pollution, or the presence of microorganisms. The origin of the cellulosic material, as well as pulping and papermaking procedures, additives, and storage conditions play a crucial role. The chemical changes occurring within paper thus involve multi-parameter processes. The purpose of this review, which mainly focuses on the most recent decade, is to provide a description of the more important changes produced by aging and an update of the new tools available for the study of paper deterioration and its conservation.

Keywords: Paper aging; Paper chemistry; Paper degradation

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INTRODUCTION

Paper as a carrier for written information was introduced in Europe in the twelfth century (Levarie 1968). It is a multi-component material, and because of its complex and varied nature, research findings in paper chemistry can be difficult to interpret, needing both chemical and physical methods to understand its characteristics. The overall behavior of paper (chemical and mechanical properties, stability, degradation, etc.) is strongly dependent upon the nature, origin, and characteristics of components as well as upon their interactions. Paper structure and its properties will also be dependent upon manufacturing processes. The paper components can be classified according to their origin, chemical structure, and function, such as fibers (composed mainly of cellulose, but also of lignin, hemicelluloses, and other minor components), mineral particles (talc, kaolin, calcium carbonate, etc.), natural sizing agents (as starch or rosin), or synthetic ones (as alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA)), colorants, and other substances.

Pre-industrial European papers often contain rag fiber and gelatin sizing. Hand-made papers from other regions may include non-wood fibers such as hemp, mulberry

inner bark, bamboo, or rice straw, as well as various starches for sizing, or no sizing at all. In addition, ink or printing media used historically in writing and illustrating may impact the long-term stability of paper.

Since the invention of the stone groundwood (SGW) process for newspapers in Germany (1845), soda pulping in England (1866), the bisulphite process in Sweden (1875), and the kraft process in Germany (1882), a new panorama opened in the production of paper, allowing its production to grow to massive levels and making possible the popularity of wood as a raw material par excellence. Nowadays, 90% of printing paper is made from wood-derived fiber, mainly from bleached kraft pulp (composed mainly of cellulose and hemicelluloses) or from mechanical pulps (lignin-containing fibers). The chemical components of the fibers, the manufacturing process, and the additives used affect, to a variable extent, the permanence of paper.

The presence of lignin in the paper, in combination with acid sizing, which remained popular in printing papers until the mid-twentieth century, means that we are facing a different reality from the case of ancient papers, but no less destructive. The emergence of neutral and alkaline sizing, and the introduction of new bleaching agents, such as chlorine dioxide, ozone, and hydrogen peroxide, among others, makes the future of our current papers, at best, difficult to predict. This is why the study of the conservation of ancient books is applicable to the documents generated in our recent history, as they suffer from the classic deterioration processes, plus other ones produced because of their manufacturing processes. From this point of view, the existence of accurate accelerated aging tests is of crucial importance to assess the possible deterioration of paper over extended periods.

Cellulose, hemicelluloses, and lignin contents in the typical plant-based raw materials are 40-50%, 15-35%, and 20-40% respectively. Lignin is an amorphous, aromatic, water insoluble, heterogeneous, three-dimensional, and cross-linked polymer. It can be considered as having been formed by random copolymers deriving from unsaturated alcohol derivatives of phenyl-propane. Lignin is not composed of exactly repeating units and can be more exactly described as a macromolecule than as a polymer; phenylpropanoid units are linked together by more than ten different types of aryl ether and carbon-carbon linkages. In addition to methoxyl groups, lignin has other functional groups, including phenyl hydroxyl, benzyl alcohol, and carbonyl. The function of this network is to provide a mechanically strong composite material with cellulose fibers. Hemicelluloses are a mixed group of both linear and branched heteropolymers mainly comprising five monomeric sugars, namely D-glucose, D-mannose, D-galactose, D-xylose, and L-arabinose. They are linked together mostly by β -1,4-glycosidic bonds, but β -1,3-, β -1,6-, α -1,2-, α -1,3-, and α -1,6-glycosidic bonds can also be found. The degree of polymerization (DP) of hemicelluloses is 100 to 200, which is much lower than that of cellulose. Hemicelluloses and lignin are covalently bound together, and this binding provides additional strength (Mukoyoshi et al. 1981; Azuma 1989; Hartley and Ford 1989; Glasser et al. 1995; Ebringerová and Heinze 2000; Wyman et al 2005). The major hemicelluloses of hardwoods and gramineous plants are glucuronoxylan and glucomannan in both, as well as galactoglucomannans, arabinoxylans, and glucuronoarabinoxylans, whereas the main types of softwood hemicelluloses are galactoglucomannans, arabinoglucuronoxylan, and arabinogalactan (Fengel and Wegener 1989; Sjöström 1993; Klemm et al. 1998).

Cellulose is a polymer consisting of linear $\beta(1-4)$ D-glucopyranosyl units. The cellulose chains have a strong tendency to aggregate to highly ordered structural entities, due to the uniformity of their chemical constitution and spatial conformation. The degree of polymerization (DP) of cellulose present in the living tree is unknown, but the size of the native molecule is often stated to be 5000 to 10000 glucopyranose units (Wise 1946; Fengel and Wegener 1989; Wyman et al 2005). Due to the regularity of chains, cellulose fibers are characterized by a relatively high degree of crystallinity. On the basis of physical and chemical behavior the supra-molecular structure of cellulose microfibrils is characterized by alternations along the chain axis between ordered crystalline and amorphous regions. The degree of polymerization of cellulose chains and the degree of crystallinity of cellulose micro-fibrils depend upon the nature and origin of the vegetable fibers (Atalla 1999; Klemm et al. 2005).

Cellulose is by no means inert. Many books and documents have become brittle. Consequently, active research concerning the permanence and durability of paper has been carried out in Europe and the United States, especially since the late 1800s.

The library, archive, and museum communities have therefore insisted that standards for paper requiring permanence be based on specific paper composition. The result has been standards that require paper to be alkaline, to contain an alkaline reserve (that is, the amount of buffer compounds capable of neutralizing acids in the future) such as calcium carbonate, and to have no more than 1% lignin content. This standard composition arose because of the excellent aging performance of very old papers that had been made with similar specifications (Roggia 1999).

Unfortunately, the conditions specified by the international standards do not always bring a complete guarantee of paper durability (Havermans 2002). There is still a high need for applied and fundamental research on paper aging and testing methods to determine the stability of papers. Although the subject has been extensively studied, the relationship between natural and artificial aging is still source of controversy, and this point is of an outstanding importance to the people working in conservation (Łojewski et al. 2010). The various aspects of natural and accelerated aging of cellulose and paper are presented and discussed in depth by Zervos (2010).

The chemical changes that occur in paper with aging involve a multi-parameter process. Different approaches to these subjects can be found in the works of various authors. Browning (1977) has described generally employed procedures that may be of utility for chemical analysis of paper, ranging from sampling to the detailed description of each method of analysis and its effectiveness. Referenced methods involve the chemical determination of the different components of the paper, based on the techniques available at the time. The book also refers to some topics of interest to conservators, such as permanence of paper and biological control. Gurnagul et al. (1993) have reviewed the literature on the factors that affect the mechanical permanence of paper. Their review covers the literature from 1895 to 1993, with an aim to reveal the anecdotal and scientific basis for the specifications outlined in the various standards for paper permanence, focused on the effect of pulp type. Zervos and Moropoulou (2006) discussed relevant topics such as accelerated ageing, sample selection and preparation, planning of the experiments, established methods for the evaluation of paper properties, various methods that have been sparingly used, and methods that had never been used at the time, but have the potential

to be applied to specific problems of the evaluation. The review of Manso and Carvalho (2009) focused on state of the art spectroscopic techniques in the field of cultural heritage conservation and characterization of paper, including the possible mechanisms of the natural or artificial degradation of the works of art. Baty et al. (2010) focused their review on deacidification, including factors affecting degradation of paper-based articles, particularly acidity and cellulose hydrolysis; deacidification agents; distribution methods; criteria for judging the success of a deacidification program, and associated or alternative treatments.

The purpose of this review, involving mainly the last decade, is to describe the more important changes produced by aging, as well as providing an overview of new tools available for the study of paper deterioration and its conservation. We present in this text: 1) a description of the most important causes of the deterioration of paper, 2) a description of the recently developed tools to study their effects, and 3) how these tools have been recently applied.

THE DETERIORATION OF PAPER

Factors Affecting the Degradation Process

Most papers suffer deterioration due to endogenous (pH, metal ions, lignin, degradation products) and exogenous (heat, humidity, pollutant gases) contributors (Laguardia et al. 2005; Strlič and Kolar 2002). The strength of paper is determined by the intrinsic strength of fibers and by the strength of interfiber bonding. Additionally, the strength of interfiber bonding depends on the relative bonded area between fibers, and of the bond strength per unit of bonded area. Beyond the possible weakening of interfiber bonds, the strength of paper decreases because of the loss of intrinsic strength of fibers due to cellulose deterioration.

Degradation of the cellulose macromolecules can be brought about with various kinds of energy input, i.e. chemical, thermal, mechanical, or radiation energy, and it can proceed via many reaction routes. The modes of cellulose degradation within paper include chemical (acid hydrolysis, enzymatic hydrolysis, alkaline degradation, and oxidative degradation), thermal (different levels of temperature), and radiation (exposure to UV/visible radiation, exposure to high-energy radiation). In nearly all modes of cellulose degradation, except perhaps that induced by high-energy radiation, cellulose supramolecular structure (crystallinity or fibrillar morphology) plays a decisive role in determining the rate and often also the course of a degradation process. A high supramolecular order of the polymer chain generally impedes degradation (Klemm et al. 1998).

The degradation produced by iron gall inks is an important factor to some historical documents. It is not included in this work, but has been treated in depth by Kolar and Strlič (2006).

Acid Catalyzed Degradation

Aging processes in paper lead to yellowing and loss of strength, in which the most prominent reaction is the hydrolytic degradation of the cellulose macromolecules (Porck 2000). The rate of the hydrolytic process is determined by the temperature, the acidity,

and the water present in the paper (paper's equilibrium moisture content). The accelerated aging of papers of pure cellulose with low initial pH and degree of polymerization results in embrittlement, with a significant loss of paper strength. This effect is mainly the result of a decrease in fiber strength, due to degradation of the cellulose caused by acid-catalyzed hydrolysis (Williams 1981).

The use of alum-rosin sizing in papermaking has been recognized as a main cause of degradation of paper (Williams 1981; Cunha 1988; Chamberlain 2007). This is because the typical aluminum compounds used in papermaking hydrolyze with the release of acidity, and acidic conditions are known to promote degradation of cellulose, reducing its degree of polymerization. In addition, acid from polluted atmospheres can enter the low-density, open, amorphous regions of the fiber and cut the polymer chain by hydrolysis (Stephens et al. 2008). The pH is the most important factor in the strength and color stability of paper. Alum plays a more important role in pH during long-term natural aging. While all the papers contained some quantities of Al, the concentration must be above certain levels in order to have a detrimental effect on the specimens. It also appears that Ca and Mg, like alum, positively impact paper stability when present in certain quantities. Studying the properties of forty naturally aged papers taken from books dating from 1477 to 1793, Stephen et al. (2008) found that when Al content was higher than 610 ppm, regardless of their alkaline earth metal content, the specimens were acidic. The same was observed when Al content was lower than 610 ppm and Ca or Mg contents below 5,000 and 840 ppm, respectively. On the contrary, when Al content was lower than 610 ppm, and the paper had Ca or Mg contents exceeding 5000 and 840 ppm, respectively, the specimens were alkaline. These results may provide insight into which elements, and at what concentrations, control long-term pH.

Paper created under neutral conditions and containing about two-thirds groundwood showed excellent mechanical stability under moist heat aging (Lyne 1995), and it could be characterized as permanent under German test standards. The predominant cause of degradation was determined to be acid hydrolysis of cellulose, which is a self-catalyzed reaction. Hemicelluloses content could be a factor contributing to the degradation rate of wood pulp fiber. It is also conceivable that rosin acids present in groundwood pulps could cause a similar attack. However, these auxiliary degradation mechanisms could only take place under acidic conditions (Lyne 1995).

Deacidifying agents provide an alkaline reserve to avoid acid hydrolysis. However, some researchers have reported a sharp decrease in DP of the cellulose and a yellowing of the paper after moist heat accelerated aging. For example, the use of sodium tetraborate provoked an increase in the pH and alkaline reserve, together with a consequent increase in ash content, but moist heat ageing of the paper involved a drastic DP decrease compared to pure water treatment (–42%) together with a remarkable yellowing (whiteness decrease – 16.7) and a drastic (nearly one third) decrease in the alkaline reserve of the paper (Botti et al. 2006).

Recent studies indicated that depolymerization by acid hydrolysis of cellulose in homogeneous acidic medium is also affected by an autocatalytic process, with a positive feedback of acid production from the degraded biopolymer. The normalized number of scissions per cellulose chain follows a sigmoid behavior, with cellulose concentration decreasing exponentially with linear and cubic time dependence (Gehlen 2009).

Alkaline Degradation of Cellulose

When subjected to strong bases, cellulose chain ends can react and undergo the well-known depolymerization reaction. The alkaline degradation mechanism of cellulose involves the following sequence: isomerization; β -alcoxy elimination (“peeling reaction”); tautomerization; and benzylic acid rearrangement to glucoisosaccharinic acid (Sjöström 1993). This reaction explains the detrimental effect on paper permanence of excessively strong bases such as calcium hydroxide particles or alcoholate (RO^-). It is to be noted that these species, when they are exposed to air, are rapidly transformed into the corresponding carbonates, which do not induce this depolymerization reaction any more. Such species are used in many mass deacidification processes.

The oxidised groups of cellulose are “potential” sites of degradation, since oxidised cellulose chains are not “actually” broken, but they can be easily degraded in both an acidic and alkaline medium, even at room temperature under mild conditions (Calvini and Gorassini 2006). This mechanism is relevant in the study of the rate of degradation of oxidised cellulose in alkaline medium, i.e., after deacidification. In this case, the overall kinetics correspond to the sum of both the actual (hydrolytic) and potential (oxidative) degradation.

An extensive review of the degradation of cellulose under alkaline conditions is presented by Knill and Kennedy (2003). The commonly identified alkaline degradation products, after neutralization, are, among many others, formic acid, acetic acid, hydroxyacetic glycolic acid, DL-glyceric acid, 3-hydroxy-DL-lactic acid, succinic acid, butyric acid, 2-hydroxybutanoic acid, 2-methyl-2,3-dihydroxypropanoic acid, 2-methyl-DL-glyceric acid, 2-methyl-3-hydroxy-DL-lactic acid, and 2,3R-dihydroxybutanoic acid, etc.

Oxidation

The oxidative degradation of cellulose is primarily induced by the presence of oxygen in the environmental air. Oxidation of the cellulose polymer introduces side groups, aldehydes, and ketones, which make the molecule more easily hydrolyzed. Free radicals generated by oxidation or by light can also cut the cellulose chain. The oxidation of cellulose also contributes to raising the concentration of acid in paper, since through photo-oxidation, the primary alcohol groups in the cellulose polymer can be oxidized to aldehydes and later to carboxylic acid species.

It is worth noting that although some colored species can be found in aged papers, it must be realized that brown lines can be generated in pure cellulose paper in distilled water. If papers are pre-washed, the process producing the tideline can be reduced, but after a few weeks the same type of tideline is likely to occur again. It can be concluded that the species responsible for the cellulose degradation and the formation of brown species are spontaneously formed (Evans and Wallis 1989). The exact mechanism is not clear at present, but can be oxidative, since water-soluble alkylhydroperoxides and free-radical species can be formed in paper and can accumulate in the tideline. As a whole, this oxidative process is supported by the basic organic chemistry, since cellulose, which is an oxygen-containing polymer, can undergo peroxy function formation by reaction with dioxygen. The migration and accumulation of such products in the tideline can result in a burst of radical chain reactions. Of course, the type of degradation occurring in the tidelines is of relevance to cellulose degradation chemistry and paper aging, since mac-

romolecular chain cleavage is observed. These experiments show that cellulose degrades slowly, but progressively even in the absence of water.

The autoxidation of cellulose in alkaline media has been followed experimentally by examining the rate of absorption of oxygen, the variation in degree of polymerization, changes in functional groups, and the chemical composition of the resulting cellulose and decomposition products of low molecular weight. A small quantity of absorbed oxygen produces a considerable change in degree of polymerization, indicating that oxidation occurs all along the cellulose macromolecule, not only at its ends. Both aldehydic and ketonic groups are formed in the oxidation of alkaline cellulose, but the carbonyl groups undergo further oxidation or other reactions. The content of carboxy-groups gradually increases with increasing duration of oxidation (Golova and Nosova 1973).

The oxidation that proceeds in an autocatalytic chain reaction (autoxidation) involves free radicals. In the autoxidation reaction scheme, transition metals play an extremely important role, as they catalyze the production of free radicals from hydroperoxides, the intermediate reaction products of atmospheric oxygen and organic matter. This catalytic reaction can be interfered with by the introduction of complexing agents (preventive antioxidants) that deactivate the transition metal, either by changing its reductive/oxidative properties or by making it inaccessible to hydroperoxides. The content of transition metals in most cellulosic materials is low enough not to present an acute problem. However, in certain inks (especially iron gall ink, or metal tannate ink) and pigments, large amounts of iron and copper are present, and these may lead to extensive localized degradation to such an extent that many historic documents are simply not legible any more (Strlič and Kolar 2002). It is worth recalling here that ferric ions are extremely acidic species, sometimes used in organic chemistry producing highly acidic intermediates such as carbenium ions (Rissoan et al. 1997).

Oxidation during thermal accelerated ageing is brought about by the action of oxygen (autoxidation). The atmospheric oxygen acts as a non-specific oxidizing agent, not directly but via various complex mechanisms, possibly by converting terminal or other existing carbonyls to peroxides, thus producing new carbonyls and carboxyls, with or without ring opening. Oxidized cellulose degrades fast by acid hydrolysis or under alkaline conditions. The reaction starts with the abstraction of a hydrogen atom bound to a carbon by a hydroxyl radical. A hydroxyalkyl radical is produced and converted by oxygen to the corresponding carbonyl structure, with the alkoxide at a β position to the carbonyl. An adjacent H^+ is then abducted by a OH^- , and a carbanion is produced, which is stabilized by a charge shift and the cleavage of the glycosidic bond (Zervos 2010). This reaction causes an immediate and detrimental effect when poorly-sized, acidic, and oxidised paper is subjected to deacidification processes.

Biological Degradation

Besides physico-chemical degradation, paper can suffer from biological attacks and degradation. Various biological contaminants are possible, even in libraries and archives, and their effect can vary as a function of environmental situations and composition of the substrate. Insects and moulds are the most frequent cause of biological problems. Treating paper-based materials against insects somewhat falls outside of this review, but data showing this effect can be found in Koestler et al. 2000.

It is worth noting that biodeterioration is the most frequently detected source of degradation of archives and books in countries located in tropical and subtropical areas. Extensive literature on paper biodeterioration caused by fungi is already available (Kowalik 1980; Szczepanowska 1986; Zyska 1997; Zotti et al. 2008). Recent studies on the biological deterioration seek the identification of isolates from fungal attacked areas, using molecular biology techniques (Michaelsen et al. 2006; Rakotonirainy et al. 2007).

Stopping this type of detrimental evolution is not easy because its origin is frequently due to improper storing conditions. *Aspergillus niger* and *Paecilomyces variotii* are representative among the most frequently found fungal strains on contaminated documents. Effective treatment of papers suffering biodeterioration caused by microorganisms can be achieved by exposing them to an atmosphere of ethylene oxide or to radiation. The former treatment, which involves handling of a dangerous gas, necessitates use of appropriate hardware, similar to the processes used in many hospitals. In addition, Valentin's (1986) research results have shown (among other things) that ethylene oxide sterilization makes paper much more susceptible to mold. In response to the need for efficient chemical, the antifungal effect of methyl and propyl paraben mixtures at different concentrations has been evaluated, and little variations in paper properties have been found. However, this technique should be more tested (Neves et al. 2009).

The application in libraries and archives of paper treatments of ionizing radiation to eradicate biodeterioration agents has been made only sporadically for the recovery of large quantities of library materials after catastrophes, such as major floods. Gamma radiation eliminates insects and fungi in the paper, it has no residual toxicity or pollution, and large volumes of material can be handled in short time (Calvo et al. 2010). The review of Magauda (2004) details the main test stages carried out to receive the authorization for the application of ionizing radiation treatment to deteriorated books and archive documents, as a physical means for their recovery from the most important biodeteriorating agents. Whereas experiments have been conducted to find the lowest gamma radiation dose needed to inactivate fungi (Dasilva et al. 2006), recent experiments have been focused on the study the effects of radiation on paper properties, especially those related to strength and appearance (D'Almeida et al. 2009, Calvo et al. 2010).

Other authors tried the removal or reduction of the microbial contamination by means of plasma treatment (Laguardia et al. 2005) with promising results.

Complete description of such treatments also falls outside of the scope of this paper, but detailed information can be found, for example in Bankole (2010), who has reviewed the current state of research on the various biological agents that could cause deterioration of paper materials and possible intervention strategies against these biotic agents.

As far as biological degradation is concerned, more than 200 moulds can be detected. From a single cell, they are able to proliferate and to produce a substratum called mycelium able to develop on most solid surfaces. However, they prefer organic substrates such as cellulose, or even gelatin, which will provide feed for development. In order to grow up, moulds produce enzymes that will chemically attack paper fibers and cleave cellulose macromolecules. However, this is not the only problem. The mould metabolism will produce acidic wastes, which will contribute to paper degradation. As has been already mentioned, acidification is in itself a source of cellulose degradation. As

a result, a mould attack will give rise to fragile and colored spots on the paper surface. The problem is the incredible resistance of the spores that are at the origin of the development of the moulds. They can be inert and “sleeping” for years and be reactivated under favorable conditions (humidity, temperature). It is worth noting that moulds can be identified based on their form of spores. Moulds require an organic food source to develop, and cellulose-containing materials such as paper provide a good substrate for their growth. The damages are irreversible and in the long term could cause the complete destruction of the documents. However, some biological studies have revealed that it is possible to reconstruct cellulose on fiber surfaces under appropriate conditions, regenerating fiber strength. These preliminary studies were carried out by the impregnation of damaged papers with proper enzymes and chemicals, but they are far from being of a practical application (Kobayashi and Shoda 1995).

When contamination by fungi is actively established in a repository, it can be difficult to eradicate the microorganisms growth, as the only efficient disinfection process currently available for documents involves ethylene oxide as explained above, and aerial disinfection of the atmosphere of the storage area. Such interventions are painstaking, time-consuming, and expensive. The prevention of mold growth is therefore a necessary task and a true challenge for curators and collection keepers. Careful control of the environment and regular cleaning are recommended in order to avoid biocontamination. However, such preventive measures are not always sufficient, especially in the case of flood disasters. While some ways to stop fungal development do exist, it must be kept in mind that as soon as a document is wet, flooded, or exposed to moisture, it is in immediate danger and must be dried, preferably freeze dried, and treated and treated by some of the mentioned techniques.

Zyska has been studying and listing fungi isolated from a full set of library materials such as books in various states, including paper parchment, leather, textiles, various glues audiovisual materials, wood, and synthetic materials. Among 84 genera, 234 different species were represented. This discovery is of concern here because some fungi involved in deterioration of library materials may behave as sources of toxic products for library staff. Actually, it was reported that about 19% of the fungi could be a source of mycotoxins (Zyska 1997). In any case, fungi seem to play a fundamental role in the deterioration of paper. For instance, an investigation on 18th century etchings in the Museo di Sant’Agostino in Genoa, Italy, showed that all the samples were contaminated with fungal entities (Zotti et al. 2008). This paper also pointed out that the collected data did not confirm the theory that states that there is a correspondence between fluorescence of the stains under UV radiation and the vitality of fungi.

A universal treatment of paper, able to deacidify, strengthen, and protect against further biological attack is still a challenge (Rakotonirainy et al. 2008).

Absorption of Atmospheric Pollutants

Atmospheric pollutants play an outstanding role in the chemical evolution of paper with aging. Most studies about this subject are dated in the decade of the 1990s. Newsprint and white wove paper grades have been used to study the absorption of SO₂ and NO₂. Both were absorbed throughout the 13- to 29-week exposures and were removed at the same rate whether present alone or as a mixture. The paper samples had a

larger capacity for uptake of SO₂ than for uptake of NO₂. Sulfate was the only sulfur-containing product observed irrespective of paper type, deacidified or not. Nitrite and nitrate, the two nitrogen-containing products observed, together accounted for all of the absorbed NO₂ (Havermans 1994; Grosjean 2006).

Reviews about the influence of atmospheric pollutants on paper permanence have pointed out that the absorption of sulfur dioxide by paper depends on many factors (Williams II and Grosjean 1992; Gurnagul and Zou 1994; Zou et al. 1998). Sulfate concentration of the books and archival materials has resulted to an extent far greater than the concentration to be expected based on the measured aluminum concentration and aluminum sulfate or alum. In addition, measurements of the nitrate concentration as a function of the age of the paper have suggested that the nitrate content of the paper increases with the age of the samples. The pollution results confirmed that sheets from mechanical pulps absorb more air pollutants and show a greater brightness loss than lignin-free sheets. Based on the reviewed literature (see below), lignin did not have any negative impact on the mechanical permanence of paper.

Lignin's Influence on the Degradation Process

Whereas bleached chemical pulp fibers are mostly composed of cellulose, with a smaller proportion of hemicelluloses, mechanical pulps fibers retain almost all of the lignin originally present in the wood. Many permanence standards, such as the ANSI standard, the ASTM standards in the USA, ISO international standard, etc., specify that permanent paper should be alkaline (as indicated by the pH of a water extract) and contain at least two percent CaCO₃ to act as a buffer (or alkaline reserve). Additionally, these standards require the virtual exclusion of lignin from the composition of the paper, because it was thought that lignin might contribute to its mechanical degradation (Arnold 1998).

Under the influence of UV radiation and also of visible light, groundwood paper yellows, the complicated structure of lignin changes, and consequently, various low-molecular weight degradation products with chromophoric properties split off. These degradation products remain in the paper and significantly influence the usability and longevity of groundwood paper. The presence of free phenolic hydroxyl groups and C- α -carbonyl groups is needed for light-induced oxidation radical reactions on lignin. Other important factors of lignin degradation are hydrolytic reactions in an acid or alkaline medium (Bukovský 2000). Light-induced oxidation of groundwood paper relies on the secondary chromophores for the color and the ability to absorb visible wavelengths of light. These species are produced by oxidative degradation reactions of lignin, and they occur in two forms. The absorption of light in certain chemical structures takes place in the lignin molecule, and these chromophoric groups are changed by the radical reactions in the presence of oxygen. This initial phase of oxidation is connected to an increase in carbonyl creation, but the splitting of the lignin molecule does not occur at this point. Another group of secondary chromophores consists of the agents of low-molecular mass formed by a complicated process of oxidation degradation and splitting-off of the lignin molecule. Even the cellulose component of paper suffers oxidative or photooxidative destruction. The extent of this destruction is very small, compared to the degradation of lignin (Bukovský and Trnková 2003).

Mechanical pulps are one of the most important products of the Canadian industry. Between 1994 and 1997, Canadian researchers carried out an ambitious research project to examine the effect of lignin on paper permanence, in both benign and polluted environments (Michaels 1997). People associated with libraries and archives have long observed that lignin seemed to cause paper yellowing, and both lignin and yellowing seemed to be connected to paper deterioration. Meanwhile, the industry has carried out research, mostly physical tests, indicating that paper yellowing does not imply simultaneous deterioration. Indeed, a study concerning the effect of lignin content on paper durability concluded that lignin contents between 0 and 28% does not produce critical loss of mechanical properties during aging (Zou et al. 1993).

The effect of sulfonic acid groups on the mechanical permanence of paper was studied by accelerated aging of thermomechanical pulp (TMP) sulfonated to different levels. Results showed that acid groups in the hydrogen form have a significant negative effect on the mechanical permanence of paper, whereas the neutralization of these groups by treatment with NaOH or CaCO₃ significantly improves it. Sulfonated mechanical pulp after washing with tap water has good mechanical permanence because the acid groups are mostly in the calcium form due to the ion exchange during washing (Zou and Gurnagul 1995). In studies concerning autoxidation of lignin-containing and lignin-free pulps, the authors found considerable discolouration for a lignin-containing pulp and proposed that the discolouration of lignin is a manifestation of its antioxidant properties (Schmidt et al. 1995).

Acidity, rather than fiber composition, is the most significant factor affecting the stability of both lignin-containing and lignin-free papers in accelerated aging tests. The addition of CaCO₃ as a buffering compound significantly improves the stability of both alkaline lignin-containing and lignin-free papers exposed to air pollutants. The optical properties of alkaline lignin-containing papers are less stable than those of alkaline lignin-free papers. Therefore, the National Standard CAN/CGSB-9.70-2000 Permanence of Paper for Records, Books and Other Documents, approved in Canada in 2000, requires permanent papers to have an alkaline reserve, a pH value in the range of 7.0 to 10.0, and the strength and performance properties as required by end-use. The standard recognizes that for most paper applications, the physical integrity of paper is the main requirement; thus the use of lignin-containing fibers should not be an issue. However, to help assuring maximum optical permanence, where required (e.g. artwork), the standard currently recommends restricting the lignin content to 1% (Zou and Gurnagul 2001).

TECHNIQUES FOR THE STUDY OF PAPER DEGRADATION

Natural Aging versus Artificial Aging

Accelerated aging of paper tests are carried out for three major purposes. The first is to establish in a conveniently short time the relative ranking of materials, or physical combinations of materials, with respect to their chemical stability or physical durability. The second is to estimate or “predict” potential long-term serviceability of material systems under expected conditions of use, and the third is to elucidate the chemical reactions involved (the degradation “mechanism”) and the physical consequences thereof (Feller

and Marina del Rey 1994). These tests are usually used to understand mechanisms of acidic hydrolysis and oxidative degradation of cellulose, hemicelluloses, and lignin (Pro-niewicz et al. 2002).

An extensive report (Porck 2000) provided an overview of the current state of affairs concerning the possibilities and limitations of artificial aging analysis. A case can be made that the results of artificial aging tests currently available do not allow for a reliable determination of the rate of paper degradation in absolute terms, and further research is needed to improve the predictive ability of such tests. There are many different accelerated aging standard techniques (i.e. ISO, TAPPI, and ASTM), involving many differences in the methods themselves, but additionally, many authors also decide to apply non-standardized conditions.

A complicating factor is the way in which the paper is exposed to the aging conditions. When paper is in stacks (i.e., books), it ages differently than do single, loose sheets. Under both accelerated and natural aging conditions, the center of a stack of paper undergoes greater deterioration than do the regions located near the outside (Porck and Teygeler 2000). This result is explained by the confinement of the degradation products in the center of the stack.

For a paper specimen to be regarded as permanent, it should exhibit a high degree of chemical stability, as evidenced by very slow deterioration. Because of the excellent aging performance of very old papers that had been made to similar specifications, most standards require paper to be alkaline, to contain an alkaline reserve such as calcium carbonate, and to have no more than 1% lignin content. ASTM International (formerly known as the American Society for Testing and Materials) has completed in 2002 a five-year research program into the aging of printing and writing papers. The research was launched in order to develop accelerated aging test methods that could be used to predict the stability of such papers to the effects of long-term natural aging. In order to meet a key goal of the program, it was necessary to show that the chemistry and physics produced by the proposed accelerated aging test methods was essentially the same as occurs in natural aging. This result has been demonstrated in the work now completed in five laboratories. They pursued three separate test methods. The means chosen to accelerate aging included elevated temperature, elevated light flux, and elevated concentration of common atmospheric pollutant gases (Arnold 2003).

Unlike in ventilated ovens, artificial ageing in confined spaces better resembles the natural ageing of paper. When the sample is confined, the reaction follows an autocatalytic pathway (Shahani et al. 2001; Zervos and Moropoulou 2005; Calvini et al. 2008). The ASTM D6819-02e3 standard for testing the accelerated aging of paper (2002), recommends using closed glass vials in order to keep the degradation products in contact with the paper, thus permitting a better simulation of the natural aging conditions inside closed books. However, kinetic studies of accelerated aging in both closed and open systems, as monitored by DP and breaking length measurements, have shown unexpectedly that no statistically meaningful difference of degradation rates can be observed. On the other hand, the pH and whiteness index values revealed a meaningful difference between the rates of aging in these systems, thus confirming the basic assumption of the ASTM test concerning the interaction of paper degradation products with the paper itself (Sawoszczuk et al. 2008).

In a project involving the testing of physical and chemical properties of six papers before and after artificial aging, comparative testing for folding endurance and pH of paper samples naturally aged for 27 years has been compared with the testing results of the same paper samples after 3 days artificial aging at $105 \pm 2^\circ\text{C}$. The authors found that the formula given in TAPPI Test Method T453 (Effect of dry heat on properties of paper and board), which theoretically equates to 25 years natural aging, was significantly inaccurate for folding endurance, and also that the degradation of paper depends to some degree on its storage environment (Batterham and Rai 2008).

The comparisons of the behavior of paper in natural versus accelerated aging are sometimes controversial. Whereas in studies about chemical modification of paper with aging, it was found that rag paper samples subjected to accelerated aging exhibited carbonyl profiles comparable to naturally aged material (Potthast et al. 2006), other authors claimed that the aging tests performed on paper material at elevated temperature and moisture content do not reflect the phenomena that occur during natural aging of paper. This conclusion has been based on the determination of the changes in the hydrogen bonding system upon sorption/desorption experiments in various conditions. The conditions used usually for the aging tests cause irreversible changes in cellulose that are different from those occurring at room temperature during natural aging. For this reason, instead of replicating natural changes, such tests may reflect artificial changes in paper rather than accelerating the same ones. In view of the results, to be able to accelerate the overall process of aging caused mainly by hydrolysis, oxygen-free pure water vapor at high temperature should be applied (Łojewski et al. 2010).

Until a more thorough understanding of wavelength and intensity effects is achieved, testing methods using high-UV and high intensity illumination cannot be considered reliable in the absence of corresponding exposure tests under ambient conditions. The accelerated aging protocols that use high-intensity broadband light or any light source with a strong UV component would significantly underestimate the light stability of papers containing mechanical pulp (McGarry et al. 2004).

Zervos (2010) presents a comprehensive review of this topic, discussing the various aspects of natural and accelerated ageing of cellulose and paper, including the correlation of natural and accelerated ageing, the chemistry of ageing, the effects of aging on the physicochemical, mechanical, optical and structural properties of cellulose, the kinetics of ageing, and the methods and applications of accelerated ageing.

Instrumental Methods for the Study of Chemical Paper Degradation

Besides paper acidity, degradation can be caused by some chemical components of paper, including metal ions, lignin, additives, degradation products, and the effects of temperature, humidity, oxygen, light, microorganisms, and pollutants. Therefore, it is essential to identify the various chemical components of paper, their impact on long-term stability, their level of degradation, and the effect of conservation treatments on them. The Library of Congress recently provided a bibliography with background references that are useful for understanding the physicochemical properties of paper, methods for testing paper properties, and the fundamental chemistry of mass deacidification (Adams 2011). Further details about these subjects are given in the review of Baty et al. (2010).

Cellulose degradation is usually characterized by the decrease of its degree of polymerization (DP), considering the essential degradation mechanisms in cellulose. The depolymerization, increasing of the number of chain scissions, is the essential mechanism of cellulose degradation by acid-hydrolysis or oxidation. DP can be determined from the measured change of the intrinsic viscosity using the Mark–Houwink equation (Ding and Wang 2008). Viscometry is fast and convenient, and is often the preferred method to estimate the average degree of polymerization (DP_v) of cellulose and its derivatives.

The intrinsic viscosity of a dilute solution of a polymer is related to its molar mass. The relation is described by the empirical Mark-Houwink-Sakurada equation:

$$[\eta] = K[\overline{M}_v]^a \quad (1)$$

The relationship between the intrinsic viscosity $[\eta]$ and the degree of polymerization (DP_v) of cellulose in CED has been formulated as (Davis 1972):

$$[\eta] = 0.91[\overline{DP}_v]^{0.85} \quad (2)$$

The value of DP_v is related to the number-average molecular weight DP_n by,

$$[\overline{DP}_v] = [\overline{DP}_n] * [(1 + a)\Gamma(1 + a)]^{1/a} \quad (3)$$

where a is the Mark-Houwink coefficient for the cellulose/CED system, and $\Gamma(a + 1)$ is the gamma function of a evaluated by reference to tabulated values (Davis 1972).

Viscosimetry is still widely used in cellulose analysis despite the multiple advantages of size-exclusion chromatography (SEC), which are chiefly the characterization of the molar mass distribution of the polymer, and the determination of the different molar mass averages. SEC also provides information about the degraded fractions, thus leading to insights in the degradation mechanisms. In SEC, the type and quality of the data and the precision in the M_r determination depend on the sensitivity of the detection method (Dupont and Mortha 2004).

There is a high demand for nondestructive or micro-destructive analytical methods that would be able to assess the current condition of the collections and their expected durability. Until a few years ago, destructive testing was the most usual approach, but nowadays non-invasive techniques also have been proven to be useful. A summary of techniques used in research related to paper conservation treatment procedures (most non-destructive or micro-destructive) in recent years, are presented in Table 1.

Mechanical Testing

In a study in which the mechanical properties of original paper samples were monitored during dry-heat and moist-heat accelerated aging tests under various experimental conditions, folding endurance was identified as a highly sensitive means for monitoring changes in paper structure (Havlinova et al. 2009). However, it is a destructive method and it requires a fairly large sample of paper. Mechanical properties of paper result not only from the spatial arrangement of the fibers and additives in the material but

also from the intrinsic qualities of the fibers themselves. This is why it is possible to follow the degradation of the material by examining the intrinsic resistance of the fibers. Thus, the wet or dry zero span tensile strength can be considered as suitable indicators of the intrinsic strength of fibers (Gurnagul and Page 1989; Batchelor 2006; Chamberlain 2007).

Table 1. Techniques Used in Research Related to Paper Conservation Treatment Procedures

Technique	Property studied	Reference
Passive sampling + chromatographic analysis	Degradation through the analysis of VOCs (aldehydes)	Fenech et al. 2010
Solid-phase micro-extraction (SPME)	Degradation through the analysis of VOCs	Pawliszyn 1997
Solid-phase micro-extraction in combination with gas chromatography-mass spectrometry (SPME/GC-MS)	Degradation through the analysis of VOCs	Strlič et al. 2007
Headspace-solid-phase micro-extraction (HS-SPME) coupled with a gas chromatography/mass spectrometry (GC/MS) HS-SPME/GC/MS	Degradation through the analysis of VOCs	Lattuati-Derieux et al. 2006
Emission cell (FLEC)	Degradation through the analysis of VOCs	Ramalho et al. 2009
Contact headspace solid-phase extraction microextraction (SPME) coupled with gas chromatography/time-of-flight mass spectrometry (GC-TOF-MS) contact headspace SPME Chiral analysis (SPME-c-GC-TOF-MS)	Degradation through the analysis of VOCs	Gaspar et al. 2010
Direct analysis in real time mass spectrometry (DART-MS)	Intact volatile, semivolatile, and nonvolatile polar organic compounds	Adams 2010
UV/vis spectroscopy	Cellulose oxidation	Łojewski et al. 2010
Fourier Transform Infrared Spectroscopy (FTIR)	(a) Study of paper and foxing; (b) determination of crystallinity changes due to aging; (c) identification of paper degradation products; (d) determination of characteristic groups (carbonyls, carboxyls, amines, conjugations, etc.); (e) study of the influence of ferric and copper ions on paper aging; (f) study of the composition and the degradation of modern and historic paper. Identification of the origin of fibers; identification of chemical composition of additives in papermaking; study of paper deterioration processes.	Proniewicz et al. 2001 Proniewicz et al. 2002 Zervos and Moropoulou 2006 Calvini et al. 2008 Manso and Carvalho 2009
Raman spectroscopy	Identification of fillers in cellulose and the determination of degradation mechanisms of cellulose	Manso and Carvalho 2009

DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy)	Effects of atmospheric pollutants on paper	Zervos and Moropoulou 2006
FTIR-PAS (FTIR Photoacoustic Spectroscopy)	(a) study of cotton-cellulose photooxidation; (b) quantitative determination of lignin, cellulose, and xylose; (c) identification of paper additives; (d) evaluation of paper deacidification and cleaning	Zervos and Moropoulou 2006
FTIR microscopy (μ FTIR)	Distribution of a compound on the paper surface	Zervos and Moropoulou 2006 Faubel et al. 2007
Scanning Electron Microscopy (SEM)	(a) observation of the morphological alterations of the fibers of old and brittle paper; (b) identification of fungi, fungi spores, and fragments; (c) identification of insects, parasites and their eggs	Zervos and Moropoulou 2006
SEM in combination with Energy Dispersive Spectroscopy (EDS)	(a) acquiring topochemical data of the paper surface, (b) the determination of the origin of paper damage; (c) the identification of additives and impurities; (d) the determination of the distribution pattern of the deacidification agent	Zervos and Moropoulou 2006
X-ray diffraction (XRD) systems μ -XRD	Elemental characterization	Duran et al. 2009
Energy dispersive X-ray fluorescence (EDXRF), Particle induced X-ray emission (PIXE), Synchrotron radiation excited X-ray fluorescence analysis (SRXRF), Wavelength dispersive X-ray fluorescence (WDXRF), Scanning electron microscopy with X-ray microanalysis (SEMEDS)	Elemental characterization	Manso and Carvalho 2009
Atomic Absorption Spectroscopy (AAS), Inductively Coupled Mass (ICP-MS) Spectroscopy	Elemental characterization	Manso and Carvalho 2009
Synchrotron radiation induced micro-X-ray fluorescence (SR- μ XRF)	Elemental characterization	Faubel et al. 2007
X-Ray Photoelectron Spectroscopy (XPS)	Characterization of polymer surfaces	Manso and Carvalho 2009
Nuclear Magnetic Resonance (NMR) spectroscopy	Evaluation of the state of conservation, gives information on some deterioration processes	Manso and Carvalho 2009
Laser-based Spectroscopy (LIBS)	Identification of surface layers such as contaminants, substrate and pigments	Manso and Carvalho 2009
Chemiluminescence	Oxidation	Malesic et al. 2002
Fluorescence	Study of foxing stains and of the brown lines at the wet-dry interface. Quantitative determination of gelatin	Zervos and Moropoulou 2006

Direct analysis in real time mass spectrometry (DART-MS)	Volatile, semivolatile, and nonvolatile polar organic compounds	Dupont et al. 2007
Capillary zone electrophoresis	Degradation products	Dupont et al. 2007 Souguir et al. 2008
Size-exclusion chromatography (SEC)	Degradation mechanisms	Dupont et al. 2002 Dupont and Mortha 2004
Fluorescence labeling with multi-detector GPC analysis according to the CCOA and FDAM method	Carbonyl and carboxyl group profiles	Potthast et al. 2006 Henniges et al. 2006
Gel Permeation Chromatography (GPC).	Saccharides determination	Kacik et al. 2009
Thermogravimetry (TG), Differential Thermal Analysis (DTA), and Differential Scanning Calorimetry (DSC)	(a) study of the thermal decomposition of cellulose, (b) evaluation of the stability of various pulps and papers; (c) study of paper aging	Zervos and Moropoulou 2006
3-D topography, topochemical mapping, and others chemical mapping	More detailed microscopic observation of the paper surface, and for additive identification	Zervos and Moropoulou 2006
Atomic Force Microscopy (AFM)	Cellulose degradation by surface topography	Piantanida et al. 2005 Coluzza et al. 2008
IR spectroscopy with statistical analysis	Thermal degradation	Puica et al. 2009

STUDIES INVOLVING THE APPLICATION OF NON-DESTRUCTIVE OR MICRO-DESTRUCTIVE TECHNIQUES

Researchers have applied various non-destructive or micro-destructive techniques, as well as combinations of them, to determine the degradation mechanisms, composition, and properties of papers. Some examples are described below.

Passive Sampling

Volatile aldehydes are produced during degradation of paper-based materials. This may result in their accumulation in archival and library repositories. Thus, passive sampling can be used as an indirect and noninvasive way to corroborate the formation of VOCs during degradation of old books. Such an approach has been carried out at ten locations in four libraries and archives, followed by chromatographic determination. Despite the highly variable sampling locations, no major differences were found, although air-filtered repositories were found to have lower concentrations, while a non-ventilated newspaper repository exhibited the highest concentrations of volatile aldehydes (formaldehyde, acetaldehyde, furfural, and hexanal). It was also evident that inside the repository and particularly inside archival boxes, the concentration of VOCs and acetic acid was much higher than the concentration of outdoor-generated pollutants (Fenech et al. 2010).

Solid Phase Microextraction

A non-invasive technique that has been gaining in popularity over the last years for the analysis of VOCs is Solid Phase Microextraction (SPME) (Pawliszyn 1997). Headspace-solid-phase microextraction (HS-SPME) coupled with a gas chromatography/mass spectrometry (GC/MS) method appears to be also a suitable method for investigating volatile compounds emitted by old books. For example, an optimized HS-SPME/GC/MS has been applied to the analysis of VOCs emitted from a groundwood pulp book naturally and artificially aged. This method, in combination with accelerated aging, enabled the characterization of 36 VOCs, (Lattuati-Derieux et al. 2006).

Detection of Diagnostic Compounds

While a number of VOCs are emitted from paper under conditions of natural or accelerated degradation, two compounds were confirmed to be of particular diagnostic value: acetic acid and furfural. A non-destructive approach for estimation of pH of historical paper using solid-phase micro-extraction in combination with gas chromatography-mass spectrometry (SPME/GC-MS), based on semi-quantitative determination of emissions of furfural from paper during degradation, has been developed. Furfural production mainly depends on the degradation pathway, and this in turn depends on sample pH (Strlič et al. 2007). Organic acids, as acetic and formic acids, and aldehydes, including acetaldehyde and formaldehyde, furfural, and methyl-furfural can be considered as relevant carbohydrates degradation compounds, whereas vanillin and guaiacol are decomposition products from lignin. VOC analysis could be a rapid diagnostic tool for the degradation and condition of their collections as well as evaluation of conservation treatments and materials analysis. Using methods of multivariate data analysis, volatile degradation products have been quantitatively correlated with properties important for the preservation of paper, including rosin, lignin and carbonyl group content, degree of polymerization of cellulose, and paper acidity (Strlič et al. 2009).

Emissions of VOCs from model papers aged in closed tubes for various periods of time were also quantified using an emission cell (FLEC) placed directly on the paper surface (Ramalho et al. 2009).

Headspace Analysis

Historical old books made from cotton/linen rag and wood pulp paper have been analyzed using the non-destructive and non-invasive contact headspace SPME-GC-TOF-MS methodology upon natural aging and accelerated degradation. Contact headspace solid-phase extraction microextraction (SPME) coupled with gas chromatography/time-of-flight mass spectrometry (GC-TOF-MS) seems to be a method capable of monitoring profiles of aging/degradation and detecting hydrocarbons, aldehydes, 2-furfural, and carboxylic acids, with the potential to measure the condition of paper. Furthermore, a new analytical tool, contact headspace SPME chiral analysis (SPME-c-GC-TOF-MS), has been used as an analytical procedure to advance the understanding of paper aging, degradation, and conservation using VOC emission (Gaspar et al. 2010).

DART-MS

Direct analysis in real time mass spectrometry (DART-MS) is a relatively new MS method that directly and quickly identifies intact volatile, semivolatile, and nonvolatile polar organic compounds in a variety of matrices without extractions, derivatizations, and chromatographic separations. Microsamples of at least 10 μg may be characterized, which means that the method may be used to analyze small paper fragments. Printing and writing papers have been characterized by using positive ion DART-MS (Adams 2010).

UV/vis and FTIR

Conjugated ketonic groups with vibrational modes around 1610 cm^{-1} have been correlated to the chromophores emerging in the range between 230 and 440 nm detected by UV/vis spectroscopy during oxidative cellulose degradation. The UV/vis and FTIR correlations, together with the theoretical charge distribution, rationalized the possible mechanism of oxidative glycosidic bond cleavage. The results support the hypothesis of the moderate oxidation of cellulose in humid atmosphere (RH 59%) at 90°C , leading mostly to conjugated diketones. Further, less intense oxidation was shown to proceed through aldehydes to carboxyls at a more advanced state of degradation. The authors proposed the hypothesis that the change in the hybridization of the carbon C(2) and C(3) atoms (from sp^3 to sp^2) together with the charge transfer from ketonic to enolic groups gives rise to the glycosidic bond cleavage (Łojewski et al. 2010).

Fourier Transform Infrared (FTIR) analysis of cellulose papers doped twenty years ago with solutions of FeCl_3 and CuCl_2 respectively and kept in polypropylene bags in the dark have demonstrated that iron-treated samples have been highly hydrolyzed and oxidized, whereas copper-treated samples have been only partly hydrolyzed and slightly oxidized (Calvini et al. 2008). This observation was in agreement with the above statement dealing with ferric ions.

The acidic hydrolysis of pure cellulose from bleached sulfite softwood and cotton linters forces changes in the hydrogen bonds that influence CCH, COH, OCH, and HCH bending vibrations, which were studied by FTIR and FTIR-Raman (Proniewicz et al. 2001). A sample of a wood-containing acid paper (75% of groundwood and 25% of bleached sulfite softwood pulp, fillers being 20% of Kaolin (w/w) and alum-rosin sizing), treated in the same conditions (21 days, 100% humidity, 100°C), have been mainly associated with the appearance of new carbonyl species, as well as the rearrangement of existing hydrogen bond network. In these conditions, paper undergoes oxidation process in which at least three new carbonyl species could be characterized (Proniewicz et al. 2002).

The development and application of a novel combination of non-destructive analytical methods based on synchrotron radiation induced micro-X-ray fluorescence (SR- μXRF) and Fourier transform infrared (FTIR) microscopy have been tried to investigate the state as well as the effectiveness of conservation procedures for historical manuscripts (Faubel et al. 2007). With the same approach, two laboratory-made X-ray diffraction (XRD) systems developed recently, the $\mu\text{-XRD}$ and XRD portable systems, were tested for the study of illuminated arabic manuscripts. Using these non-destructive techniques, the presence of calcite and rutile; also, hematite, goethite, cinnabar, brass, anatase, and barite has been detected in the various colors (Duran et al. 2009). X-ray Fluorescence

(XRF) is nowadays a standard technique across the paper industry, used to determine oxide concentrations, coating thickness and composition, and other important paper chemistries.

Chemiluminescence

Chemiluminescence is the emission of light with limited emission of heat, as the result of a chemical reaction. This technique has been applied for the study of the oxidation of cellulose (Strlič and Kolar 2005; Rychlý et al. 2006; Kočar et al. 2008), lignin containing papers (Rychlý 2005), and hemicelluloses (Matisovarychla et al. 2008).

To study the role of transition metals in oxidative degradation of cellulose, degradation experiments with model papers and studies of hydroxyl radical production in solution have been performed with Fe, Cu, Mn, Co, Cr, Ni, and Zn. Results were evaluated by DP and chemiluminescence. The experiments provide strong evidence that the role of transition metals during the oxidative degradation of cellulose is catalytic. A correlation between the behavior of transition metals in solution and in paper was established at low contents of transition metals in paper (Selih et al. 2007).

Capillary Zone Electrophoresis

Capillary zone electrophoresis with direct and indirect UV detection was used for the characterization of several classes of degradation products (low-molar mass organic acids, aromatic lignin derivatives, and simple carbohydrates) from old books. In this case, the compounds found in the books and in the model paper after accelerated aging were identical to those produced during their lifespan through natural aging. Considerable amounts of vanillic acid and a major quantity of arabinose have been found in lignocellulosic papers, whereas a significant presence of glucose has been found in pure cellulose papers, and low-molar mass organic acids were found in all papers, as they arose from both cellulose and hemicelluloses degradation (Dupont et al. 2007).

Recently, a fundamental study made by capillary zone electrophoresis with indirect UV detection established that a specific degradation can occur in paper, giving rise to an increased production of organic acids and hydroperoxides. More importantly, it has been demonstrated that the paper that suffered water migration was more sensitive to degradation. This research has given a deeper insight in the process of cellulose degradation by natural oxidation. This formation of brown lines in paper at the wet-dry interface in cellulosic substrate has been described in several papers for a long time (Souguir et al. 2008).

Viscometry

Classical viscosimetry, although destructive, remains widely used as a method for determining the degradation mechanism of cellulose, because it requires no sophisticated equipment. For example, the effect of carbonyl groups on the stability of cellulose was determined by studying the aging behavior of seven different cellulose pulps deacidified using either calcium or magnesium bicarbonate. A linear correlation was obtained between carbonyl content and degradation of cellulose pulps during seven days of accelerated aging. Oxidation of the terminal reducing units of cellulose with molecular oxygen in alkaline medium leads, mainly, to the next lower aldonic acid and formate, supposedly

via ionization of the intermediate enediol, which may imply a pH dependency of the reaction. During the course of the reaction, superoxide ($O^{\bullet-}$) is formed. Although it is believed that $O^{\bullet-}$ is not able to extract hydrogen atom from glucose, it may undergo disproportionation, and the hydroperoxides thus formed may lead to hydroxyl radical formation (Malesic et al. 2002).

Size Exclusion Chromatography

In studies of polymer degradation, Size Exclusion Chromatography (SEC) has become regarded as an analytical method of choice when subtle effects are to be followed and only small amounts of samples are available. Since SEC provides comprehensive information on both the direct values and the distribution of molecular mass, it becomes especially effective in resolving paper degradation kinetics. SEC of cellulose is very efficient to demonstrate that a chemical agent can cleave the macromolecule, or to show whether the neutralizing agents protect the macromolecule from chain cleavage (Dupont et al. 2002). Together with viscosimetric measurements of the degree of polymerization, SEC is especially effective in tracing the hydrolysis progress during paper degradation. However, for the lignin-containing papers for which viscosimetry fails, it becomes the only method available (Łojewski et al. 2010).

Some of the main causes for the formation of carbonyl and carboxyl groups in cellulose fibers are isolation and purification procedures during papermaking process, besides natural aging. This applies in particular to cellulosic pulps from wood, which have undergone a number of processing steps to be freed from lignin, hemicelluloses, and extractives. Carbonyl and carboxyl group profiles have been studied by a method combining group-selective fluorescence labeling with multi-detector GPC analysis according to the CCOA (Carbazole-9-carboxylic acid [2-(2-aminooxy-ethoxy)ethoxy]amide) and FDAM (9H-Fluoren-2-yl-diazomethane) methods, respectively. In naturally aged rag paper, samples present relatively high amount of carbonyl groups. From the amount of reducing ends, as estimated from M_n , it was calculated that the amount of keto functions, which are related to oxidative processes, was about 50% of the total carbonyls, while the remaining half was attributed to reducing ends that are naturally present or resulting from hydrolysis. Rag paper samples having experienced accelerated aging exhibited carbonyl profiles comparable to naturally aged material. Results showed that during natural aging, oxidation preferentially occurred in the low MW region. The progressive degradation of rag paper produced higher amounts of acidic low-molecular weight material, with consequently increased amounts of carboxyl groups in this region (Potthast et al. 2006).

A study of the accelerated aging of newsprint paper has been performed at 98°C during 60 days. Degradation was studied by viscometry, Gel Permeation Chromatography (GPC), and saccharides determination. The authors found that in the first stages of the accelerated aging the decrease of DP is fast, and the degradation takes place homogeneously (hydrolysis is a dominant process). Later, the decrease of DP is slower, and the other types of reactions take place (oxidation, crosslinking). The saccharides amount in the paper diminished, and the hemicelluloses are degraded faster than cellulose. The ratio of hemicelluloses to glucose decreased linearly (Kacık et al. 2009).

Thermal Analysis

Thermal analysis, and in particular TGA, makes it possible to monitor the degradation level in paper, because it performs a complete investigation of the thermal behaviour of paper and the influence of the main degradative agents (light, heating, oxygen, and enzymes) on it. In a study concerning the thermal stability of paper and its components (Princi et al. 2008), in order to evaluate the effect of the artificial weathering treatments, TGA and SEM observations have been performed to follow the degradative phenomena. Different papers were evaluated, such as filter paper (Whatman), newsprint, and paperboards. TGA curves of the weathered samples showed changes with respect to the starting materials; in particular, the chemical oxidation appears as the most degradative action in respect to the other physical treatments (Princi et al. 2008).

Atomic Force Microscopy

Atomic Force Microscopy (AFM) has been used to characterize the relationship between surface topographies and cellulose degradation patterns. It is a tool to study fiber degradations, as they appear on paper surface, aiming, in the mid-term, at assessment of a micro-destructive technique capable of providing qualitative and semi-quantitative information on deterioration and aging. AFM is sensitive to deterioration and offers a new insight into the morphological behavior of the cellulose, for instance in the surface of cotton fibers during degradation. Moreover, even if AFM is not sufficient to determine the nature of the process in as much detail as the destructive evaluation can provide, it does allow for a micro-destructive quantitative distinction to be made between the initial and final stage (Piantanida et al. 2005; Coluzza et al. 2008).

Use of Statistics

Some progress in elucidating the complex mechanisms of thermal degradation of aged cellulose has been accomplished by combining IR spectroscopy experimental data with statistical analysis. The statistical processing of the experimental results made it possible to establish some acceptable regression models describing dependence between the half time and the temperature at which the paper support is kept (Puica et al. 2009).

Non-destructive Metals Analysis

Other analytical techniques available for micro-sample and non-destructive analysis of metals in paper and ink are detailed in Strlič et al. (2006).

Forensic Applications

Instrumental chemical analysis has recently found a very interesting field of utilization in the forensic applications related to paper. For example, infrared spectroscopy and wide angle X-ray diffraction (WAXD) have been used as non-destructive techniques for the discrimination of paper samples in forensic applications. All the samples out of a population of 19 papers, indistinguishable by visual examination, have been discriminated. These two techniques made it possible to detect the variations in the structure brought about by different processing parameters, manufacturing conditions and formulation of additives (Causin et al. 2010).

Advances Analytical Methods

Among others, ICPMS, XRF, LA-ICPMS, IRMS, LA-ICP-TOF-MS, X-ray fluorescence, laser desorption ionization MS direct analysis in real time (DART) MS, ESI-MS, UV/Vis spectrophotometry, LDI-MS, CE coupled to a diode array, easy ambient sonic-spray ionization mass spectrometry (EASI-MS), pyrolysis GC/MS, GC/MS and microspectrophotometry, Raman and SERS, LDI-MS, microattenuated total reflectance FT-IR, TOF-SIMS, microspectrochemical analysis techniques of LA-ICPMS and LIBS, LA-ICPMS, TXRF, and graphite furnace atomic absorption spectroscopy (GFAAS), have been employed for this use and could be good examples for conservation purposes. A complete review of modern analytical methods for the study of different aspects of paper and inks for forensic applications is presented in Brettell et al. (2011).

Physical test methods, unfortunately, have not had the same degree of innovation. Most of the techniques are destructive and require large samples. Only ultrasonic testing has been used as non-destructive determination of paper elastic stiffness properties (Mark et al. 2001; Knutson et al. 2007).

CONCLUSIONS

Even if the main chemical reactions occurring in paper, mainly affecting cellulose and other polysaccharides, are well identified, this survey shows that there are many useful analyses, some of which have recently been developed, that can improve our knowledge of the chemical changes that take place in paper during aging. Until a few years ago, sampling and analysis with destructive techniques was the most usual procedure, but nowadays, non-invasive analytical techniques also been proven to be useful. Moreover, it is clear that the combination of several techniques can bring important information. However, the highly complex instruments used are mostly very expensive, and are not available in all laboratories. For this reason, some classical destructive techniques are still valid. In contrast, no options have emerged to replace mechanical tests, which are destructive and require large samples, so much remains to be done in this area. This is an area where classical statistical methods and multivariable analysis can contribute. There is a high demand for nondestructive or micro-destructive analytical and physical methods that would be able to assess the current condition of the collections and their expected durability. The specialists in conservation need a deeper understanding of the relationship between the aged books and documents during their chemical evolution with aging, and the mechanical properties of the supporting paper. Despite the many recent existing works dealing with accelerated aging of paper, a clear correspondence between artificial and natural aging is still missing, and this point is of an outstanding importance to the people working in conservation.

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